

COAL CONVERSION IN CO/WATER:  
THE ROLES OF PYROLYSIS AND PHENOLICS IN CONVERSION

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Introduction

The relationship of coal liquefaction behavior to coal structure has been a subject of study for several years, particularly with respect to loss of coal oxygen (1). Traditionally, the liquefaction behavior of a coal has been defined in terms of its product solubility in a particular solvent such as pyridine, benzene, or tetrahydrofuran. However, an inherent complication in trying to relate reactivity to liquefaction, defined in terms of product solubility, is that a variety of factors contribute to the product's overall solubility in a given solvent

The chemical nature of the product, i.e., the sum of its aromaticity, heteroatom content, and functional group distribution, will determine its solubility to a large degree. The molecular weight distribution of the product will also play an important role. The complex interactions evolving from the various possible combinations of these specific factors thus rule out the development of any reasonably simple correlation between structure and reactivity. And it follows that product solubility is not necessarily a good relative measure of a coal's reactivity in a given conversion medium, particularly among a set of coals of substantially different chemical constitution.

This work is dealt with here in work with the separate CO/water and N<sub>2</sub>/water treatments of several coals from the Eastern Province of the U.S. The research focuses on a development of some insight into effects of oxygen functionality on conversion, with particular focus on phenolic functionality.

Background and Approach

Two requirements for a study aimed at developing a correlation between coal structure and reactivity are (i) a diagnostic for conversion that is free from problems associated with solubility, and (ii) a means of separating the reductive conversion chemistry from the parallel pyrolytic chemistry also in effect.

Most common liquefaction media employ an H-donor component such as tetralin, which transfers hydrogen to the coal. In such a medium the coal is reduced and degraded to yield a more soluble, lower molecular weight product. In principle, the more hydrogen added to the coal, the greater the overall solubility of the products. However, given the complexities of solubility just noted, the quantity of hydrogen transferred to the coal would seem to be a better measure of its reactivity, or its propensity toward reduction.

Yet even with this approach there are complicating factors. Conversion, of course, always accompanies thermal treatment of coal in H-donor media. Accordingly there is no way to separate or distinguish products that are a result of pyrolytic processes, and independent of conversion. Additionally, conversions in such media yield products contaminated by the solvent through chemical incorporation.

Conversions conducted in a carbon monoxide/water system circumvent both of these problems. First, the medium is totally inorganic and provides an organic product derived solely from the coal. Second,  $N_2$  can be used in place of CO to provide a product that has not been reduced, but has been otherwise subjected to the same time-temperature conditions as the product obtained using CO. This product can be considered as a "blank run" and can provide a basis for comparison. Finally, and perhaps most significantly, carbon monoxide/water and tetralin share some mechanistic features; thus insights gained from studies using CO/H<sub>2</sub>O can be confidently applied to conversion in tetralin (2).

The results of several published studies show that conversions in CO/H<sub>2</sub>O generally decrease with increasing carbon content of the starting coal. Appell et al., using synthesis gas (H<sub>2</sub> and CO) and water, found that a lignite gave higher conversion than a bituminous coal (3). Ouchi and Takemura, using CO/H<sub>2</sub>O and a cobalt-molybdenum catalyst, found that conversion decreased with increasing carbon content for a series of coals ranging from 50% to 90% carbon (4). Oelert and Siekmann found that conversion increased with increasing O/C ratio of the starting material (5). These results, taken together, suggest that oxygen functionalities strongly influence the conversion behavior of the coal. These past studies have dealt with materials of widely different origin and geologic age, however, and any structure-reactivity relationship derived from such studies can provide only limited mechanistic insight. In the work reported here we have confined our effort to a series of Eastern Province coals to minimize this factor.

### Experimental

The elemental analyses of the coals are shown in Table 1. The coals were ground and sieved under dry  $N_2$  until all coal passed a 100-mesh sieve. The coals were then dried under vacuum at 105°C overnight before use. All reactions were performed in a 300-mL Magne-Drive-stirred Hastelloy C autoclave. The autoclave was loaded with 5 g of dry coal and 30 g of H<sub>2</sub>O that was previously adjusted to a pH of 13.0 with solid KOH. The system was sealed, purged with  $N_2$ , purged again with either  $N_2$  or CO, and then filled with either  $N_2$  or CO (500 psig).

Table 1  
ELEMENTAL ANALYSIS (Wt%) OF EASTERN PROVINCE COALS (dmmf)<sup>a</sup>

PSOC No.	Seam	C	H	N	S	O <sup>b</sup>	O <sub>OH</sub> <sup>c</sup>	Mineral Matter
278	Ohio No. 9	81.5	6.0	1.1	5.4	6.0	4.7	18.0
306	Ohio No. 12	82.4	6.1	1.8	2.6	7.1	3.4	34.1
307	Ohio No. 12A	83.1	5.9	1.7	3.6	5.7	3.9	25.6
1099	Pittsburgh	86.8	5.7	1.4	2.2	3.9	2.8	12.8
268	Lyons	88.0	5.3	1.4	1.6	3.7	2.5	6.2

<sup>a</sup>Our determinations.

<sup>b</sup>By difference.

<sup>c</sup>Determined by Given and coworkers by O-acetylation (8).

The coal was converted by heating the autoclave to 400°C (± 5°C) for 20 min. Maximum pressures attained ranged from 3500 to 4000 psig. The heat-up and cool-down times were each about one hour.

Quantitative analyses of the product gases CO, CO<sub>2</sub>, and H<sub>2</sub> were made by gas chromatography using known standards. The aqueous phase was pipetted from the

autoclave, and suspended material was filtered if necessary. The nonvolatile coal products were quantitatively removed from the autoclave with tetrahydrofuran (THF) and transferred to a round-bottom flask. The THF was removed by rotary evaporation. 400 mL of toluene was added, and the mixture was refluxed for 2 h with a Dean-Stark trap.

Azeotropic distillation removed any water. After cooling, the mixture was filtered to separate the toluene soluble material (TS) from the toluene-insoluble material (TI). The toluene was removed from the filtrate by rotary evaporation. Both the TS and TI fractions were dried overnight at 80°C and weighed. Carbon, hydrogen, and nitrogen analysis of the products were made using a Control Equipment 241 microanalyzer.

### Results

In earlier work we described our use of CO/water conversion for bituminous coals and discussed how the conversions to toluene-soluble products were dependent on the initial pH of the aqueous medium (6). We have found that, at least for Illinois No. 6 coal, about 50% of the starting oxygen in the coal is lost under conversion conditions (7). This O is loosely bound and is lost rapidly whether CO or N<sub>2</sub> is used. We concluded that under conversion conditions there is a rapidly produced pyrolytic product, which is then the true precursor to subsequently formed upgraded products.

The CO/water conversion parallels the water-gas-shift reaction (WGSR).



An intermediate in the WGSR, most likely formate, is principally responsible for conversion, rather than the H<sub>2</sub> derived from the shift reaction.

In the work discussed here, both the toluene-solubilities and the H/C of the products from runs in both N<sub>2</sub>/H<sub>2</sub>O and CO/H<sub>2</sub>O were measured and compared for each coal. The results are interpreted in terms of the phenolic contents of the starting coals.

Toluene-Soluble Products. All coals were converted by heating to 400°C for 20 min in either CO/H<sub>2</sub>O or N<sub>2</sub>/H<sub>2</sub>O at a starting pH of 13.0. The conversions to toluene-soluble material (TS) in both N<sub>2</sub>/H<sub>2</sub>O and CO/H<sub>2</sub>O were measured for each coal. The results are shown in Table 2. Conversion to %TS is defined on a dry, mineral-matter-free basis and is calculated as

$$\% \text{TS} = (\text{wt TS} / \text{wt dmmf coal}) \times 100 \quad 2)$$

The N<sub>2</sub>-runs yielding results due to only pyrolytic chemistry, surprisingly show for some of the coals substantial liberation of TS material. The difference in conversions in the two media yields the net conversion due to reduction alone:

$$\% \text{TS}(\text{net}) = \% \text{TS}(\text{CO}/\text{H}_2\text{O}) - \% \text{TS}(\text{N}_2/\text{H}_2\text{O}) \quad 3)$$

The conversions do not take into account production of light hydrocarbon gases. The major hydrocarbon gases were always methane and ethane; however, they accounted for less than 2% of the total amount of carbon charged to the reactor in both CO/H<sub>2</sub>O and N<sub>2</sub>/H<sub>2</sub>O runs, as determined by gas chromatography.

Carbon and Hydrogen Analyses of TS and TI Products. Carbon recoveries based on the C-content of the starting coal ranged from 70% to 94% for runs in N<sub>2</sub>/H<sub>2</sub>O and from 89% to 98% for runs in CO/H<sub>2</sub>O. Thus, recoveries were consistently better in CO/H<sub>2</sub>O runs.

Table 2  
TOLUENE SOLUBILITIES AND H/C RATIOS OF PRODUCTS

PSOC No.	$x_{TS}$		$x_{TS, net}$	$H/C_{TS}$		$H/C_{TL}$		$H/C_{Composite}$		$\Delta H/100\text{ C}$
	$N_2/H_2O$	$CO/H_2O$		$N_2/H_2O$	$CO/H_2O$	$N_2/H_2O$	$CO/H_2O$	$N_2/H_2O$	$CO/H_2O$	
278	21	85	58 <sup>a</sup>	1.14	1.09	0.76	0.79	0.84	1.06	21
	--	72		--	1.09	--	0.81	--	1.04	
306	16	38	22	1.18	1.03	0.70	0.85	0.78	0.92	14
307	10	44	34	1.10	1.04	0.69	0.84	0.75	0.94	19
1099	10	44	34	1.10	1.02	0.70	0.71	0.74	0.86	12
268	10	35	26 <sup>b</sup>	1.03	0.98	0.64	0.68	0.68	0.79	11
	8	--		1.07	--					

<sup>a</sup>Using the average of the  $CO/H_2O$  values.

<sup>b</sup>Using the average of the  $N_2/H_2O$  values.

The H/C ratios of the products are listed in Table 2. For the  $N_2/H_2O$  runs, there is a net loss of hydrogen relative to carbon, whereas in  $CO/H_2O$  runs there is a net gain. Based on our view that the true precursor of the conversion products is the initially formed product from pyrolysis, we can calculate the net gain in hydrogen per 100 carbon atoms by the composite values for the TS and TI fractions.

$$\Delta H/100C = [H/C_{comp}(CO/H_2O) - H/C_{comp}(N_2/H_2O)] \times 100 \quad 4)$$

### Discussion

The yields of TS in the runs with  $N_2$ /water shown in Table 2 are unexpected, particularly in view of some of the pyrolytic hydrogen losses. The  $N_2$ -result with PSOC 278 yielding a product with 21% toluene solubility is striking, as is the high H/C ratio of the TS fraction. The very high TS value for the  $CO$ /water runs is therefore in part due to the large component resulting from pyrolysis. This result demonstrates the important role pyrolysis can play in conversion and the need to separate pyrolysis and reduction in liquefaction studies.

For PSOC 278 the loss of starting hydrogen in the  $N_2$ -runs is minimal, suggesting a possible reciprocal relationship between pyrolytic H-loss and pyrolytic conversion. The results for PSOC 306, however, rule against any direct link between the two, since there is a significant 16% TS fraction from  $N_2$ /water, while the H/C ratio decreases by about 11%.

The phenolic contents of a number of coals including those studied here have been established by Given and coworkers (8). Figure 1 plots the %TS solubilities (right-hand ordinate) for the  $CO$ /water conversions of the Eastern Province coals as a function of these values. The figure shows a rough correlation between the two components. However, the trend of increasing TS values with increasing  $O_{OH}$  is set by the extreme solubility value of around 80% for PSOC 278. If that result is excluded, there appears to be no real correlation over an  $O_{OH}$  spread of almost a factor of 2.

One problem with this attempted correlation is the narrow range of TS values for most of the coals. The complication introduced through considering product solubility as the diagnostic is clearly apparent here. Another part of the problem is the use of the full solubility, and ignoring the fact that there are significant levels of pyrolytic formation of TS fractions for some of the coals.

A better view of the conversion due solely to reduction can be derived from considering the  $H/100C$  values from in Table 2. These data are also presented in Figure 1, and in this case a very good linear relationship is obtained. For the Eastern Province coals, the line fits the equation

$$\Delta H/100C = 4.8 O_{OH}/100C + 0.5 \quad 5)$$

with a correlation coefficient of 0.97. The excellent fit confirms the need to avoid solubility as the diagnostic for conversion, and to correct liquefaction data for pyrolytic reactions. Thus the H/C ratio of the original coal is not a proper characteristic for comparison.

The fact that the extended line passes near the origin suggests that a mechanistic correlation exists between the hydrogen uptake by the coal, and the phenolic content. Phenol functions thus seem to play a direct role in the specific reduction chemistry. The slope of the line dictates that 5 hydrogens are added to the coal structure for each phenolic group, and at present we have no scheme to explain that value. We have noted that the phenolic content stays reasonably constant with conversion and that unaccounted or loosely bound oxygen represented the major source of lost oxygen (7). It therefore seems that, although phenol functions in the coal may be the key to the introduction of hydrogen into coal

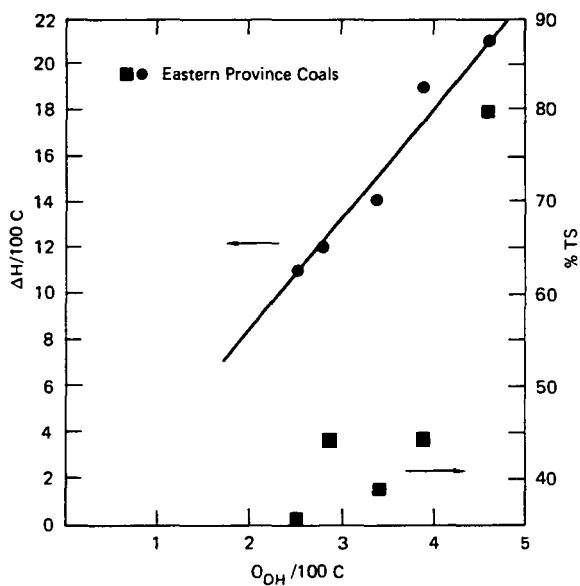
during CO/water conversion, they are not directly removed by the conversion chemistry.

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FIGURE 1 PLOT OF HYDROGEN UPTAKE AND  $\% \text{ TS}$   
VERSUS PHENOLIC OXYGEN

The circles refer to  $\Delta H/100\text{ C}$ ; the squares refer to  $\% \text{ TS}$ .